(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 098 151 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
31.03.2004 Bulletin 2004/14

(51) Int Cl.[7]: **F25J 3/04**

(21) Application number: **00123862.5**

(22) Date of filing: **02.11.2000**

(54) **Cryogenic air separation process using multicomponent refrigerant**

Tieftemperaturverfahren zur Luftzerlegung mit mehrkomponentem Kühlmedium

Procédé cryogénique de séparation de l'air utilisant un mélange réfrigérant

(84) Designated Contracting States:
DE ES FR GB IT

(30) Priority: **03.11.1999 US 432211**

(43) Date of publication of application:
09.05.2001 Bulletin 2001/19

(60) Divisional application:
03029302.1

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(56) References cited:
EP-A- 1 016 840
GB-A- 1 120 712
US-A- 4 420 946

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Description

Technical Field

[0001] This invention relates generally to the separation of feed air by cryogenic rectification to produce, inter alia, gaseous nitrogen and gaseous oxygen.

Background Art

[0002] The production of gaseous nitrogen and gaseous oxygen by the cryogenic rectification of feed air requires the provision of a significant amount of refrigeration to drive the separation. Generally such refrigeration is provided by the turboexpansion of a process stream, such as a portion of the feed air. While this conventional practice is effective, it is limiting because an increase in the amount of refrigeration inherently affects the operation of the overall process. It is therefor desirable to have a cryogenic air separation process wherein the provision of the requisite refrigeration is independent of the flow of process streams for the system.

[0003] One method for providing refrigeration for a cryogenic air separation system which is independent of the flow of internal system process streams is to provide the requisite refrigeration in the form of exogenous cryogenic liquid brought into the system. Unfortunately such a procedure is very costly.

[0004] In EP-A-1 016 840, which is prior art under Art. 54(3) EPC, there is disclosed a process for the production of gaseous nitrogen and gaseous oxygen by the cryogenic rectification of feed air comprising:

(A) compressing a multicomponent refrigerant fluid, cooling the compressed multicomponent refrigerant fluid, expanding the cooled, compressed multicomponent refrigerant fluid, and warming the expanded multicomponent refrigerant fluid by indirect heat exchange with said cooling compressed multicomponent refrigerant fluid and also with feed air to produce cooled feed air;

(B) passing the cooled feed air into a higher pressure cryogenic rectification column and separating the feed air by cryogenic rectification within the higher pressure cryogenic rectification column into nitrogen-enriched fluid and oxygen-enriched fluid;

(C) passing nitrogen-enriched fluid and oxygen-enriched fluid into a lower pressure cryogenic rectification column, and separating the fluids passed into the lower pressure column by cryogenic rectification to produce nitrogen-rich fluid and oxygen-rich fluid;

(D) withdrawing nitrogen-rich fluid from the upper portion of the lower pressure column and recovering the withdrawn nitrogen-rich fluid as product gaseous nitrogen; and

(E) withdrawing oxygen-rich fluid from the lower portion of the lower pressure column and recovering the withdrawn oxygen-rich fluid as product gaseous oxygen.

[0005] In GB-A-1 120 712 there is provided a system for separation of a multicomponent gaseous mixture such as air using a distillation column, in which a closed cycle heat pump is employed to provide reboil and condensation for the column, the heat pump cycle involving a cold compressor and in which inter and/or aftercooling for the compressor is provided from an external refrigeration source. The external refrigerant may be liquefied gas or a mixture of gases, such as liquefied hydrocarbons or oxygen, or vapor arising from boiling thereof.

[0006] Accordingly it is an object of this invention to provide an improved cryogenic air separation process wherein the provision of the requisite refrigeration for the separation is independent of the flow of process streams.

[0007] It is another object of this invention to provide a cryogenic air separation process wherein the provision of the requisite refrigeration for the separation is independently and efficiently provided to the system.

Summary Of The Invention

[0008] The above objects are attained by the present invention, one aspect of which is

a process for the production of gaseous nitrogen and gaseous oxygen by the cryogenic rectification of feed air as defined in claim 1.

[0009] As used herein the term "column" means a distillation or fractionation column or zone, i.e. a contacting column or zone, wherein liquid and vapor phases are countercurrently contacted to effect separation of a fluid mixture, as for example, by contacting of the vapor and liquid phases on a series of vertically spaced trays or plates mounted within the column and/or on packing elements such as structured or random packing. For a further discussion of distillation columns, see the Chemical Engineer's Handbook, fifth edition, edited by R. H. Perry and C. H. Chilton, McGraw-Hill Book Company, New York, Section 13, The Continuous Distillation Process.

[0010] The term "double column" is used to mean a higher pressure column having its upper portion in heat exchange

relation with the lower portion of a lower pressure column. A further discussion of double columns appears in Ruheman "The Separation of Gases", Oxford University Press, 1949, Chapter VII, Commercial Air Separation.

[0011] Vapor and liquid contacting separation processes depend on the difference in vapor pressures for the components. The high vapor pressure (or more volatile or low boiling) component will tend to concentrate in the vapor phase whereas the low vapor pressure (or less volatile or high boiling) component will tend to concentrate in the liquid phase. Distillation is the separation process whereby heating of a liquid mixture can be used to concentrate the more volatile component(s) in the vapor phase and thereby the less volatile component(s) in the liquid phase. Partial condensation is the separation process whereby cooling of a vapor mixture can be used to concentrate the volatile component(s) in the vapor phase and thereby the less volatile component(s) in the liquid phase. Rectification, or continuous distillation, is the separation process that combines successive partial vaporizations and condensations as obtained by a countercurrent treatment of the vapor and liquid phases. The countercurrent contacting of the vapor and liquid phases can be adiabatic or nonadiabatic and can include integral (stagewise) or differential (continuous) contact between the phases. Separation process arrangements that utilize the principles of rectification to separate mixtures are often interchangeably termed rectification columns, distillation columns, or fractionation columns. Cryogenic rectification is a rectification process carried out at least in part at temperatures at or below 150 degrees Kelvin (K).

[0012] As used herein the term "indirect heat exchange" means the bringing of two fluid streams into heat exchange relation without any physical contact or intermixing of the fluids with each other.

[0013] As used herein the term "expansion" means to effect a reduction in pressure.

[0014] As used herein the term "product gaseous nitrogen" means a gas having a nitrogen concentration of at least 99 mole percent.

[0015] As used herein the term "product gaseous oxygen" means a gas having an oxygen concentration of at least 90 mole percent.

[0016] As used herein the term "feed air" means a mixture comprising primarily oxygen, nitrogen and argon, such as ambient air.

[0017] As used herein the terms "upper portion" and "lower portion" mean those sections of a column respectively above and below the mid point of the column.

[0018] As used herein the term "variable load refrigerant" means a multicomponent fluid, i.e. a mixture of two or more components in proportions such that the liquid phase of those components undergoes a continuous and increasing temperature change between the bubble point and the dew point of the mixture. The bubble point of the mixture is the temperature, at a given pressure, wherein the mixture is all in the liquid phase but addition of heat will initiate formation of a vapor phase in equilibrium with the liquid phase. The dew point of the mixture is the temperature, at a given pressure, wherein the mixture is all in the vapor phase but extraction of heat will initiate formation of a liquid phase in equilibrium with the vapor phase. Hence, the temperature region between the bubble point and the dew point of the mixture is the region wherein both liquid and vapor phases coexist in equilibrium. In the practice of this invention the temperature differences between the bubble point and the dew point for the multicomponent refrigerant fluid is at least 10°K, preferably at least 20°K and most preferably at least 50°K.

[0019] As used herein the term "fluorocarbon" means one of the following: tetrafluoromethane (CF_4), perfluoroethane (C_2F_6), perfluoropropane (C_3F_8), perfluorobutane (C_4F_{10}), perfluoropentane (C_5F_{12}), perfluoroethene (C_2F_4), perfluoropropene (C_3F_6), perfluorobutene (C_4F_8), perfluoropentene (C_5F_{10}), hexafluorocyclopropane (cyclo-C_3F_6) and octafluorocyclobutane (cyclo-C_4F_8).

[0020] As used herein the term "hydrofluorocarbon" means one of the following: fluoroform (CHF_3), pentafluoroethane (C_2HF_5), tetrafluoroethane ($C_2H_2F_4$), heptafluoropropane (C_3HF_7), hexafluoropropane ($C_3H_2F_6$), pentafluoropropane ($C_3H_3F_5$), tetrafluoropropane ($C_3H_4F_4$), nonafluorobutane (C_4HF_9), octafluorobutane ($C_4H_2F_8$), undecafluoropentane (C_5HF_{11}), methyl fluoride (CH_3F), difluoromethane (CH_2F_2), ethyl fluoride (C_2H_5F), difluoroethane ($C_2H_4F_2$), trifluoroethane ($C_2H_3F_3$), difluoroethene ($C_2H_2F_2$), trifluoroethene (C_2HF_3), fluoroethene (C_2H_3F), pentafluoropropene (C_3HF_5), tetrafluoropropene ($C_3H_2F_4$), trifluoropropene ($C_3H_3F_3$), difluoropropene ($C_3H_4F_2$), heptafluorobutene (C_4HF_7), hexafluorobutene ($C_4H_2F_6$) and nonafluoropentene (C_5HF_9).

[0021] As used herein the term "fluoroether" means one of the following: trifluoromethyoxy-perfluoromethane (CF_3-O-CF_3), difluoromethoxy-perfluoromethane (CHF_2-O-CF_3), fluoromethoxy-perfluoromethane (CH_2F-O-CF_3), difluoromethoxy-difluoromethane (CHF_2-O-CHF_2), difluoromethoxy-perfluoroethane (CHF_2-O-C_2F_5), difluoromethoxy-1,2,2,2-tetrafluoroethane (CHF_2-O-C_2HF_4), difluoromethoxy-1,1,2,2-tetrafluoroethane (CHF_2-O-C_2HF_4), perfluoroethoxy-fluoromethane (C_2F_5-O-CH_2F), perfluoromethoxy-1,1,2-trifluoroethane (CF_3-O-$C_2H_2F_3$), perfluoromethoxy-1,1,2-trifluoroethane (CF_3O-$C_2H_2F_3$), cyclo-1,1,2,2-tetrafluoropropylether (cyclo-$C_3H_2F_4$-O-), cyclo-1,1,3,3-tetrafluoropropylether (cyclo-$C_3H_2F_4$-O-), perfluoromethoxy-1,1,2,2-tetrafluoroethane (CF_3-O-C_2HF_4), cyclo-1,1,2,3,3-pentafluoropropylether (cyclo-C_3H_5-O-), perfluoromethoxy-perfluoroacetone (CF_3-O-CF_2-O-CF_3), perfluoromethoxy-perfluoroethane (CF_3-O-C_2F_5), perfluoromethoxy-1,1,2,2-tetrafluoroethane (CF_3-O-C_2HF_4), perfluoromethoxy-2,2,2-trifluoroethane (CF_3-O-$C_2H_2F_3$), cyclo-perfluoromethoxy-perfluoroacetone (cyclo-CF_2-O-CF_2-O-CF_2-) and cyclo-perfluoropropylether (cyclo-C_3F_6-O).

[0022] As used herein the term "atmospheric gas" means one of the following: nitrogen (N_2), argon (Ar), krypton (Kr), xenon (Xe), neon (Ne), carbon dioxide (CO_2), oxygen (O_2) and helium (He).

[0023] As used herein the term "non-toxic" means not posing an acute or chronic hazard when handled in accordance with acceptable exposure limits.

[0024] As used herein the term "non-flammable" means either having no flash point or a very high flash point of at least 600°K.

[0025] As used herein the term "low-ozone-depleting" means having an ozone depleting potential less than 0.15 as defined by the Montreal Protocol convention wherein dichlorofluoromethane (CCl_2F_2) has an ozone depleting potential of 1.0.

[0026] As used herein the term "non-ozone-depleting" means having no component which contains a chlorine, bromine or iodine atom.

[0027] As used herein the term "normal boiling point" means the boiling temperature at 1 standard atmosphere pressure, i.e. 14.696 pounds per square inch absolute.

Brief Description Of The Drawings

[0028] Figure 1 is a schematic representation of a conventional cryogenic air separation plant wherein a single multicomponent refrigerant circuit is used to produce the refrigeration for the separation.

[0029] Figure 2 is a schematic representation of a preferred embodiment of the invention wherein two multicomponent refrigerant circuits, a high temperature circuit and a low temperature circuit, are used to produce the refrigeration for the system.

Detailed Description

[0030] In general, the invention comprises the decoupling of the refrigeration generation for a cryogenic air separation process from the flow of process streams for the process. This enables one to change the amount of refrigeration put into the process without requiring a change in flow of process streams. For example, one may now operate the process to produce large amounts of liquid product in addition to the gaseous products without burdening the system with excessive turboexpansion of process streams to generate the refrigeration necessary to produce such liquid product.

[0031] The invention will be described in greater detail with reference to the Drawings. In Figure 1 there is illustrated a conventional cryogenic air separation plant having three columns, a double column having higher and lower pressure columns, and an argon sidearm column.

[0032] Referring now to Figure 1, feed air 60 is compressed by passage through base load compressor 30 to a pressure generally within the range of from 275.8 to 1379 kPa (40 to 200 pounds per square inch absolute (psia)). Resulting compressed feed air 61 is cooled of the heat of compression in aftercooler 31 and resulting feed air stream 62 is then cleaned of high boiling impurities such as water vapor, carbon dioxide and hydrocarbons by passage through purifier 132. Purified feed air stream 63 is cooled by passage through main heat exchanger 1 by indirect heat exchange with return streams and by refrigeration generated by the multicomponent refrigerant fluid circuit as will be more fully described below, and then passed as stream 65 into higher pressure column 10 which is operating at a pressure generally within the range of from 275.8 to 1379 kPa (40 to 200 psia). Within higher pressure column 10 the feed air is separated by cryogenic rectification into nitrogen-enriched vapor and oxygen-enriched liquid. Nitrogen-enriched vapor is withdrawn from the upper portion of higher pressure column 10 in stream 71 and condensed in main condenser 4 by indirect heat exchange with boiling lower pressure column bottom liquid. Resulting nitrogen-enriched liquid 72 is returned to column 10 as reflux as shown by stream 73. A portion 74 of the nitrogen-enriched liquid 72 is passed from column 10 to subcooler 3 wherein it is subcooled to form subcooled stream 77 which is passed into the upper portion of column 11 as reflux. If desired, a portion 75 of stream 73 may be recovered as product liquid nitrogen. Also, if desired, a portion (not shown) of nitrogen-enriched vapor stream 71 may be recovered as product high pressure nitrogen gas.

[0033] Oxygen-enriched liquid is withdrawn from the lower portion of higher pressure column 10 in stream 69 and passed to subcooler 2 wherein it is subcooled. Resulting subcooled oxygen-enriched liquid 70 is then divided into portion 93 and portion 94. Portion 93 is passed into lower pressure column 11 and portion 94 is passed into argon column condenser 5 wherein it is at least partially vaporized. The resulting vapor is withdrawn from condenser 5 in stream 95 and passed into lower pressure column 11. Any remaining oxygen-enriched liquid is withdrawn from condenser 5 and then passed into lower pressure column 11.

[0034] Lower pressure column 11 is operating at a pressure less than that of higher pressure column 10 and generally within the range of from 103.4 to 1241 kPa (15 to 180 psia). Within lower pressure column 11 the various feeds into that column are separated by cryogenic rectification into nitrogen-rich vapor and oxygen-rich liquid. Nitrogen-rich vapor is withdrawn from the upper portion of column 11 in stream 83, warmed by passage through heat exchangers 3, 2 and 1, and recovered as product gaseous nitrogen in stream 86 having a nitrogen concentration of at least 99 mole percent,

preferably at least 99.9 mole percent, and most preferably at least 99.999 mole percent. For product purity control purposes a waste stream 87 is withdrawn from column 11 from a level below the withdrawal point of stream 83, warmed by passage through heat exchangers 3, 2 and 1, and removed from the system in stream 90. Oxygen-rich liquid is partially vaporized in the lower portion of column 11 by indirect heat exchange with condensing nitrogen-enriched vapor in main condenser 4 as was previously described. Resulting oxygen-rich vapor is withdrawn from the lower portion of column 11 in stream 81 having an oxygen concentration generally within the range of from 90 to 99.9 mole percent. Oxygen-rich vapor in stream 81 is warmed by passage through main heat exchanger 1 and recovered as product gaseous oxygen in stream 82.

[0035] Fluid comprising oxygen and argon is passed in stream 91 from lower pressure column 11 into argon column 12 wherein it is separated by cryogenic rectification into argon-richer fluid and oxygen-rich fluid. Oxygen-richer fluid is passed from the lower portion of column 12 in stream 92 into lower pressure column 11. Argon-richer fluid is passed from the upper portion of column 12 as vapor into argon column condenser 5 wherein it is condensed by indirect heat exchange with the aforesaid subcooled oxygen-enriched liquid. Resulting argon-richer liquid is withdrawn from condenser 5. A portion of the argon-richer liquid is passed into argon column 12 as reflux and another portion is recovered as product argon having an argon concentration generally within the range of from 95 to 99.9 mole percent as shown by stream 96.

[0036] There will now be described in greater detail the operation of the multicomponent refrigerant fluid. circuit which serves to generate preferably all the refrigeration passed into the cryogenic rectification plant thereby eliminating the need for any turboexpansion of a process stream to produce refrigeration for the separation, thus decoupling the generation of refrigeration for the cryogenic air separation process from the flow of process streams, such as feed air, associated with the cryogenic air separation process.

[0037] The following description illustrates the multicomponent refrigerant fluid system for providing refrigeration throughout the primary heat exchanger 1. Multicomponent refrigerant fluid in stream 105 is compressed by passage through recycle compressor 32 to a pressure generally within the range of from 413.7 to 6895 kPa (60 to 1000 psia) to produce compressed refrigerant fluid 106. The compressed refrigerant fluid is cooled of the heat of compression by passage through aftercooler 33 and may be partially condensed. The resulting multicomponent refrigerant fluid in stream 101 is then passed through heat exchanger 1 wherein it is further cooled and generally is at least partially condensed and may be completely condensed. The resulting cooled, compressed multicomponent refrigerant fluid 102 is then expanded or throttled through valve 103. The throttling preferably partially vaporizes the multicomponent refrigerant fluid, cooling the fluid and generating refrigeration. For some limited circumstances, dependent on heat exchanger conditions, the compressed fluid 102 may be subcooled liquid prior to expansion and may remain as liquid upon initial expansion. Subsequently, upon warming in the heat exchanger, the fluid will have two phases. The pressure expansion of the fluid through a valve would provide refrigeration by the Joule-Thomson effect, i.e. lowering of the fluid temperature due to pressure expansion at constant enthalpy. However, under some circumstances, the fluid expansion could occur by utilizing a two-phase or liquid expansion turbine, so that the fluid temperature would be lowered due to work expansion.

[0038] Refrigeration bearing multicomponent two phase refrigerant fluid stream 104 is then passed through heat exchanger 1 wherein it is warmed and completely vaporized thus serving by indirect heat exchange to cool stream 101 and also to transfer refrigeration into the process streams within the heat exchanger, including feed air stream 63, thus passing refrigeration generated by the multicomponent refrigerant fluid refrigeration circuit into the cryogenic rectification plant to sustain the cryogenic air separation process. The resulting warmed multicomponent refrigerant fluid in vapor stream 105 is then recycled to compressor 32 and the refrigeration cycle starts anew. In the multicomponent refrigerant fluid refrigeration cycle while the high pressure mixture is condensing, the low pressure mixture is boiling against it, i.e. the heat of condensation boils the low-pressure liquid. At each temperature level, the net difference between the vaporization and the condensation provides the refrigeration. For a given refrigerant component combination, mixture composition, flowrate and pressure levels determine the available refrigeration at each temperature level.

[0039] The multicomponent refrigerant fluid contains two or more components in order to provide the required refrigeration at each temperature. The choice of refrigerant components will depend on the refrigeration load versus temperature for the specific process. Suitable components will be chosen depending upon their normal boiling points, latent heat, and flammability, toxicity, and ozone-depletion potential.

[0040] One preferable embodiment of the multicomponent refrigerant fluid useful in the practice of this invention comprises at least two components from the group consisting of fluorocarbons, hydrofluorocarbons and fluoroethers.

[0041] Another preferable embodiment of the multicomponent refrigerant fluid useful in the practice of this invention comprises at least one component from the group consisting of fluorocarbons, hydrofluorocarbons and fluoroethers, and at least one atmospheric gas.

[0042] Another preferable embodiment of the multicomponent refrigerant fluid useful in the practice of this invention comprises at least two components from the group consisting of fluorocarbons, hydrofluorocarbons and fluoroethers,

and at least two atmospheric gases.

[0043] Another preferable embodiment of the multicomponent refrigerant fluid useful in the practice of this invention comprises at least one fluoroether and at least one component from the group consisting of fluorocarbons, hydrofluorocarbons, fluoroethers and atmospheric gases.

[0044] In one preferred embodiment the multicomponent refrigerant fluid consists solely of fluorocarbons. In another preferred embodiment the multicomponent refrigerant fluid consists solely of fluorocarbons and hydrofluorocarbons. In another preferred embodiment the multicomponent refrigerant fluid consists solely of fluorocarbons and atmospheric gases. In another preferred embodiment the multicomponent refrigerant fluid consists solely of fluorocarbons, hydrofluorocarbons and fluoroethers. In another preferred embodiment the multicomponent refrigerant fluid consists solely of fluorocarbons, fluoroethers and atmospheric gases.

[0045] The multicomponent refrigerant fluid useful in the practice of this invention may contain other components such as hydrochlorofluorocarbons. Preferably, the multicomponent refrigerant fluid contains no hydrochlorofluorocarbons. In another preferred embodiment of the invention the multicomponent refrigerant fluid contains no hydrocarbons. Most preferably the multicomponent refrigerant fluid contains neither hydrochlorofluorocarbons nor hydrocarbons. Most preferably the multicomponent refrigerant fluid is non-toxic, non-flammable and non-ozone-depleting and most preferably every component of the multicomponent refrigerant fluid is either a fluorocarbon, hydrofluorocarbon, fluoroether or atmospheric gas.

[0046] The invention is particularly advantageous for use in efficiently reaching cryogenic temperatures from ambient temperatures. Tables 1-8 list preferred examples of multicomponent refrigerant fluid mixtures useful in the practice of this invention. The concentration ranges given in the Tables are in mole percent.

TABLE 1

COMPONENT	CONCENTRATION RANGE
C_5F_{12}	5-25
C_4F_{10}	0-15
C_3F_8	10-40
C_2F_6	0-30
CF_4	10-50
Ar	0-40
N_2	10-80

TABLE 2

COMPONENT	CONCENTRATION RANGE
$C_3H_3F_5$	5-25
C_4F_{10}	0-15
C_3F_8	10-40
CHF_3	0-30
CF_4	10-50
Ar	0-40
N_2	10-80

TABLE 3

COMPONENT	CONCENTRATION RANGE
$C_3H_3F_5$	5-25
$C_3H_2F_6$	0-15
$C_2H_2F_4$	0-20
C_2HF_5	5-20
C_2F_6	0-30
CF_4	10-50
Ar	0-40
N_2	10-80

TABLE 4

COMPONENT	CONCENTRATION RANGE
CHF_2-O-C_2HF_4	5-25
C_4H_{10}	0-15
CF_3-O-C_2F_3	10-40
C_2F_6	0-30
CF_4	10-50
Ar	0-40
N_2	10-80

TABLE 5

COMPONENT	CONCENTRATION RANGE
$C_3H_3F_5$	5-25
$C_3H_2F_6$	0-15
CF_3-O-C_2F_3	10-40
CHF_3	0-30
CF_4	0-25
Ar	0-40
N_2	10-80

TABLE 6

COMPONENT	CONCENTRATION RANGE
$C_2HCl_2F_3$	5-25
C_2HClF_4	0-15
C_3F_8	10-40
CHF_3	0-30
CF_4	0-25
Ar	0-40
N_2	10-80

TABLE 7

COMPONENT	CONCENTRATION RANGE
$C_2HCl_2F_3$	5-25
C_2HClF_4	0-15
CF_3-O-C_2F_3	10-40
CHF_3	0-30
CF_4	0-25
Ar	0-40
N_2	10-80

TABLE 8

COMPONENT	CONCENTRATION RANGE
$C_2HCl_2F_3$	5-25
C_2HClF_4	0-15
$C_2H_2F_4$	0-15

TABLE 8 (continued)

COMPONENT	CONCENTRATION RANGE
C_2HF_5	10-40
CHF_3	0-30
CF_4	0-25
Ar	0-40
N_2	10-80

[0047] In a preferred embodiment of the invention each of the two or more components of the refrigerant mixture has a normal boiling point which differs by at least 5 degrees Kelvin, more preferably by at least 10 degrees Kelvin, and most preferably by at least 20 degrees Kelvin, from the normal boiling point of every other component in the refrigerant mixture. This enhances the effectiveness of providing refrigeration over a wide temperature range which encompasses cryogenic temperatures. In a particularly preferred embodiment of the invention, the normal boiling point of the highest boiling component of the multicomponent refrigerant fluid is at least 50°K, preferably at least 100°K, most preferably at least 200°K, greater than the normal boiling point of the lowest boiling component of the multicomponent refrigerant fluid.

[0048] Figure 2 illustrates a preferred embodiment of the invention in accordance with which more than one multicomponent refrigerant fluid circuit is employed. In the specific embodiment illustrated in Figure 2 there are two multicomponent refrigerant fluid circuits employed, a high temperature circuit and a low temperature circuit. The multicomponent refrigerant fluid in the high temperature circuit will contain primarily higher boiling components and the multicomponent refrigerant fluid in the low temperature circuit will contain primarily lower boiling components. By the use of multiple multicomponent refrigerant fluid circuits such as the arrangement illustrated in Figure 2, one can more effectively avoid any problems associated with the freezing of any component, thus improving the efficiency of the systems. The numerals of Figure 2 are the same as those of Figure 1 for the common elements and these common elements will not be described again in detail. The cryogenic air separation system illustrated in Figure 2 does not include an argon column so that subcooled oxygen-enriched liquid 70 is passed directly into lower pressure column 11.

[0049] Referring now to Figure 2, high temperature multicomponent refrigerant fluid in stream 110 is compressed by passage through recycle compressor 35 to a pressure generally within the range of from 413.7 to 3447 kPa (60 to 500 psia) to produce compressed high temperature refrigerant fluid 111. The compressed refrigerant fluid is cooled of the heat of compression by passage through aftercooler 36 and may be partially condensed. The resulting high temperature multicomponent refrigerant fluid in stream 112 is then passed through heat exchanger 1 wherein it is further cooled and preferably is at least partially condensed and may be completely condensed. The cooled, compressed high temperature multicomponent refrigerant fluid 107 is then expanded or throttled through valve 108. The throttling preferably partially vaporizes the high temperature multicomponent refrigerant fluid, cooling the fluid and generating refrigeration. Resulting high temperature multicomponent refrigerant fluid in stream 109 has a temperature generally within the range of from 120 to 270K, preferably from 120 to 250K. Stream 109 is then passed through heat exchanger 1 wherein it is warmed by indirect heat exchange with the cooling high temperature multicomponent refrigerant fluid in stream 112, with feed air in stream 63, and also with the multicomponent refrigerant fluid circulating in the other multicomponent refrigerant fluid circuit, termed the low temperature multicomponent refrigerant circuit, which is operating in a manner similar to that described in conjunction with the embodiment illustrated in Figure 1. In the multiple circuit embodiment illustrated in Figure 2, the low temperature multicomponent refrigerant fluid in stream 104 has a temperature generally within the range of from 80 to 200K, preferably from 80 to 150K.

[0050] Table 9 presents illustrative examples of high temperature (column A) and low temperature (column B) multicomponent refrigerant fluids which may be used in the practice of the invention in accordance with the embodiment illustrated in Figure 2. The compositions are in mole percent.

TABLE 9

COMPONENT	COMPOSITION (A)	COMPOSITION (B)
$C_2HCl_2F_3$	5-30	0-25
C_2HClF_4	0-30	0-15
$C_2H_2F_4$	10-30	0-15
C_2HF_5	0-30	10-40
CHF_3	0-30	0-30
CF_4	0-30	10-50

TABLE 9 (continued)

COMPONENT	COMPOSITION (A)	COMPOSITION (B)
Ar	0-15	0-40
N_2	0-15	10-80

[0051] The components and their concentrations which make up the multicomponent refrigerant fluids useful in the practice of this invention preferably are such as to form a variable load multicomponent refrigerant fluid and preferably maintain such a variable load characteristic throughout the whole temperature range of the method of the invention. This markedly enhances the efficiency with which the refrigeration can be generated and utilized over such a wide temperature range. The defined preferred group of components has an added benefit in that they can be used to form fluid mixtures which are non-toxic, non-flammable and low or non-ozone-depleting. This provides additional advantages over conventional refrigerants which typically are toxic, flammable and/or ozone-depleting.

[0052] One preferred variable load multicomponent refrigerant fluid useful in the practice of this invention which is non-toxic, non-flammable and non-ozone-depleting comprises two or more components from the group consisting of C_5F_{12}, CHF_2-O-C_2HF_4, C_4HF_9, $C_3H_3F_5$, C_2F_5-O-CH_2F, $C_3H_2F_6$, CHF_2-O-CHF_2, C_4F_{10}, CF_3-O-$C_2H_2F_3$, C_3HF_7, CH_2F-O-CF_3, $C_2H_2F_4$, CHF_2-O-CF_3, C_3F_8, C_2HF_5, CF_3-O-CF_3, C_2F_6, CHF_3, CF_4, O_2, Ar, N_2, Ne and He.

[0053] Although the invention has been described in detail with reference to certain preferred embodiments, those skilled in the art will recognize that there are other embodiments of the invention within the scope of the claims.

Claims

1. A process for the production of gaseous nitrogen and gaseous oxygen by the cryogenic rectification of feed air comprising:

(A) compressing a high temperature multicomponent refrigerant fluid (110), cooling the compressed high temperature multicomponent refrigerant fluid (112), expanding the cooled, compressed high temperature multicomponent refrigerant fluid (107), and warming the expanded high temperature multicomponent refrigerant fluid (109) by indirect heat exchange with said cooling compressed high temperature multicomponent refrigerant fluid (112) and with low temperature multicomponent refrigerant fluid (101, 104) and also with feed air (63);

(B) compressing low temperature multicomponent refrigerant fluid (105), cooling the compressed low temperature multicomponent refrigerant fluid (101), expanding the cooled, compressed low temperature multicomponent refrigerant fluid (102), and warming the expanded low temperature multicomponent refrigerant fluid (104) by indirect heat exchange with said cooling compressed low temperature multicomponent refrigerant fluid (112) and also with feed air (63) to produce cooled feed air (65);

(C) passing the cooled feed air (65) into a higher pressure cryogenic rectification column (10) and separating the feed air by cryogenic rectification within the higher pressure cryogenic rectification column into nitrogen-enriched fluid and oxygen-enriched fluid;

(D) passing nitrogen-enriched fluid (71) and oxygen-enriched fluid (69) into a lower pressure cryogenic rectification column (11), and separating the fluids passed into the lower pressure column by cryogenic rectification to produce nitrogen-rich fluid and oxygen-rich fluid;

(E) withdrawing nitrogen-rich fluid (83) from the upper portion of the lower pressure column (11) and recovering the withdrawn nitrogen-rich fluid as product gaseous nitrogen (86); and

(F) withdrawing oxygen-rich fluid (81) from the lower portion of the lower pressure column (11) and recovering the withdrawn oxygen-rich fluid as product gaseous oxygen (82);

wherein the temperature of the expanded high temperature multicomponent refrigerant fluid (109) is within the range of from 120 to 270 K, and the temperature of the expanded low temperature multicomponent refrigerant fluid (104) is within the range of from 80 to 200 K, and wherein the multicomponent refrigerant fluids (105, 110) contain no hydrocarbons.

2. The process of claim 1 wherein the multicomponent refrigerant fluids (105, , 110) comprise at least two components from the group consisting of fluorocarbons, hydrofluorocarbons and fluoroethers.

3. The process of claim 1 wherein the multicomponent refrigerant fluids (105, 110) comprise at least one component from the group consisting of fluorocarbons, hydrofluorocarbons and fluoroethers and at least one atmospheric gas.

4. The process of claim 1 wherein the multicomponent refrigerant fluids (105, 110) comprise at least two components from the group consisting of fluorocarbons, hydrofluorocarbons and fluoroethers and at least two atmospheric gases.

5. The process of claim 1 wherein the multicomponent refrigerant fluids (105, 110) comprise at least one fluoroether and at least one component from the group consisting of fluorocarbons, hydrofluorocarbons, fluoroethers and atmospheric gases.

6. The process of claim 1 wherein the normal boiling point of the highest boiling component of the multicomponent refrigerant fluids (105, 110) is at least 50 K greater than the normal boiling point of the lowest boiling component of the multicomponent refrigerant fluid.

7. The process of claim 1 wherein the multicomponent refrigerant fluids (105, 110) comprise at least two components from the group consisting of C_5F_{12}, CH_2-O-C_2HF_4, C_4HF_9, $C_3H_3F_5$, C_2F_5-O-CH_2F, $C_3H_2F_6$, CHF_2-O-CHF_2, C_4F_{10}, CF_3-O-$C_2H_2F_3$, C_3HF7, CH_2F-O-CF_3, $C_2H_2F_4$, CHF2-O-CF_3 C_3F_8, C_2HF_5, CF_3-O-CF_3, C2F_6, CHF_3, CF_4, O_2, Ar, N_2, Ne and He.

Patentansprüche

1. Verfahren zum Erzeugen von gasförmigem Stickstoff und gasförmigem Sauerstoff mittels Tieftemperaturrektfikation von Einsatzluft, bei welchem:

(A) ein Hochtemperaturmehrkomponentenkühlfluid (110) verdichtet wird, das verdichtete Hochtemperaturmehrkomponentenkühlfluid (112) gekühlt wird, das gekühlte, verdichtete Hochtemperaturmehrkomponentenkühlfluid (107) expandiert wird, und das expandierte Hochtemperaturmehrkomponentenkühlfluid (109) mittels indirektem Wärmeaustausch mit dem abkühlenden verdichteten Hochtemperaturmehrkomponentenkühlfluid (112) und mit Niedrigtemperaturmehrkomponentenkühlfluid (101, 104) sowie mit Einsatzluft (63) erwärmt wird;

(B) Niedrigtemperaturmehrkomponentenkühlfluid (105) verdichtet wird, das verdichtete Niedrigtemperaturmehrkomponentenkühlfluid (101) gekühlt wird, das gekühlte verdichtete Niedrigtemperaturmehrkomponentenkühlfluid (102) expandiert wird und das expandierte Niedrigtemperaturmehrkomponentenkühlfluid (104) mittels indirektem Wärmeaustausch mit dem abkühlenden verdichteten Niedrigtemperaturmehrkomponentenkühlfluid (112) sowie mit Einsatzluft (63) erwärmt wird, um gekühlte Einsatzluft (65) zu erzeugen;

(C) die gekühlte Einsatzluft (65) in eine bei höherem Druck arbeitende Tieftemperaturrektifikationskolonne (10) geleitet wird und die Einsatzluft mittels Tieftemperaturrektifikation innerhalb der bei höherem Druck arbeitenden Tieftemperaturrektifikationskolonne in mit Stickstoff angereichertes Fluid und mit Sauerstoff angereichertes Fluid zerlegt wird;

(D) mit Stickstoff angereichertes Fluid (71) und mit Sauerstoff angereichertes Fluid (69) in eine bei niedrigerem Druck arbeitende Tieftemperaturrektifikationskolonne (11) geleitet werden, und die in die bei niedrigerem Druck arbeitende Kolonne geleiteten Fluide mittels Tieftemperaturrektifikation zerlegt werden, um stickstoffreiches Fluid und sauerstoffreiches Fluid zu erzeugen;

(E) stickstoffreiches Fluid (83) von dem oberen Bereich der bei niedrigerem Druck arbeitenden Kolonne (11) abgezogen wird und das abgezogene stickstoffreiche Fluid als gasförmiger Produktstickstoff (86) gewonnen wird; und

(F) sauerstoffreiches Fluid (81) von dem unteren Bereich der bei niedrigerem Druck arbeitenden Kolonne (11) abgezogen wird und das abgezogene sauerstoffreiche Fluid als gasförmiger Produktsauerstoff (82) gewonnen wird;

wobei die Temperatur des expandierten Hochtemperaturmehrkomponentenkühlfluids (109) im Bereich von 120 bis 270 K liegt und die Temperatur des expandierten Niedrigtemperaturmehrkomponentenkühlfluids (104) im Bereich von 80 bis 200 K liegt und wobei die Mehrkomponentenkühlfluide (105, 110) keine Kohlenwasserstoffe enthalten.

2. Verfahren nach Anspruch 1, bei welchem die Mehrkomponentenkühlfluide (105, 110) mindestens zwei Komponenten aus der aus Fluorkohlenstoffen, Fluorkohlenwasserstoffen und Fluorethern bestehenden Gruppe enthalten.

3. Verfahren nach Anspruch 1, bei welchem die Mehrkomponentenkühlfluide (105, 110) mindestens eine Komponente aus der aus Fluorkohlenstoffen, Fluorkohlenwasserstoffen und Fluorethern bestehenden Gruppe sowie mindestens ein atmosphärisches Gas enthalten.

4. Verfahren nach Anspruch 1, bei welchem die Mehrkomponentenkühlfluide (105, 110) mindestens zwei Komponenten aus der aus Fluorkohlenstoffen, Fluorkohlenwasserstoffen und Fluorethern bestehenden Gruppe sowie mindestens zwei atmosphärische Gase enthalten.

5. Verfahren nach Anspruch 1, bei welchem die Mehrkomponentenkühlfluide (105, 110) mindestens einen Fluorether und mindestens eine Komponente aus der aus Fluorkohlenstoffen, Fluorkohlenwasserstoffen, Fluorethern und atmosphärischen Gasen bestehenden Gruppe enthalten.

6. Verfahren nach Anspruch 1, bei welchem der normale Siedepunkt der am höchsten siedenden Komponente der Mehrkomponentenkühlfluide (105, 110) mindestens 50 K höher liegt als der normale Siedepunkt der am niedrigsten siedenden Komponente des Mehrkomponentenkühlfluids.

7. Verfahren nach Anspruch 1, bei welchem die Mehrkomponentenkühlfluide (105, 110) mindestens zwei Komponenten aus der aus C_5F_{12}, CHF_2-O-C_2HF_4, C_4HF_9, $C_3H_3F_5$, C_2F_5-O-CH_2F, $C_3H_2F_6$, CHF_2-O-CHF_2, C_4F_{10}, CF_3-O-$C_2H_2F_3$, C_3HF_7, CH_2F-O-CF_3, $C_2H_2F_4$, CHF_2-O-CF_3, C_3F_8, C_2HF_5, CF_3-O-CF_3, C_2F_6, CHF_3, CF_4, O_2, Ar, N_2, Ne and He bestehenden Gruppe aufweisen.

Revendications

1. Procédé pour la production d'azote gazeux et d'oxygène gazeux par rectification cryogénique d'air d'alimentation, comprenant les étapes consistant :

(A) à comprimer un fluide réfrigérant multiconstituant à haute température (110), à refroidir le fluide réfrigérant multiconstituant à haute température comprimé (112), à provoquer l'expansion du fluide réfrigérant multiconstituant à haute température comprimé refroidi (107), et à réchauffer le fluide réfrigérant multiconstituant à haute température expansé (109) par échange indirect de chaleur avec ledit fluide réfrigérant multiconstituant à haute température comprimé se refroidissant (112) et avec le fluide réfrigérant multiconstituant à basse température (101, 104) et également avec l'air d'alimentation (63) ;
(B) à comprimer le fluide réfrigérant multiconstituant à basse température (105), à refroidir le fluide réfrigérant multiconstituant à basse température comprimé (101), à provoquer l'expansion du fluide réfrigérant multiconstituant à basse température comprimé refroidi (102) et à réchauffer le fluide réfrigérant multiconstituant à basse température expansé (104) par échange indirect de chaleur avec ledit fluide réfrigérant multiconstituant à basse température comprimé se refroidissant (112) et également avec l'air d'alimentation (63) pour produire de l'air d'alimentation refroidi (65) ;
(C) à faire passer l'air d'alimentation refroidi (65) dans une colonne de rectification cryogénique à plus haute pression (10) et à séparer l'air d'alimentation par rectification cryogénique dans la colonne de rectification cryogénique à plus haute pression en un fluide enrichi en azote et en un fluide enrichi en oxygène ;
(D) à faire passer le fluide enrichi en azote (71) et le fluide enrichi en oxygène (69) dans une colonne de rectification cryogénique à pression plus basse (11), et à séparer les fluides passés dans la colonne à pression plus basse par rectification cryogénique pour produire un fluide riche en azote et un fluide riche en oxygène ;
(E) à décharger le fluide riche en azote (83) de la partie supérieure de la colonne à pression plus basse (11) et à recueillir le fluide riche en azote déchargé comme produit consistant en azote gazeux (86) ; et
(F) à décharger le fluide riche en oxygène (81) de la partie inférieure de la colonne à pression plus basse (11) et à recueillir le fluide riche en oxygène déchargé comme produit consistant en oxygène gazeux (82) ;

dans lequel la température du fluide réfrigérant multiconstituant à haute température expansé (109) est comprise dans l'intervalle de 120 à 270 K, et la température du fluide réfrigérant multiconstituant à basse température expansé (104) est comprise dans l'intervalle de 80 à 200 K, et dans lequel les fluides réfrigérants multiconstituants (105, 110) ne contiennent aucun hydrocarbure.

2. Procédé suivant la revendication 1, dans lequel les fluides réfrigérants multiconstituants (105, 110) comprennent au moins deux constituants choisis dans le groupe consistant en des fluorocarbones, des hydrofluorocarbones et des éthers fluorés.

3. Procédé suivant la revendication 1, dans lequel les fluides réfrigérants multiconstituants (105, 110) comprennent au moins un constituant choisi dans le groupe consistant en des fluorocarbones, des hydrofluorocarbones et des éthers fluorés et au moins un gaz atmosphérique..

4. Procédé suivant la revendication 1, dans lequel les fluides réfrigérants multiconstituants (105, 110) comprennent au moins deux constituants choisis dans le groupe consistant en des fluorocarbones, des hydrofluorocarbones et des éthers fluorés et au moins deux gaz atmosphériques.

5. Procédé suivant la revendication 1, dans lequel les fluides réfrigérants multiconstituants (105, 110) comprennent au moins un éther fluoré et au moins un constituant choisi dans le groupe consistant en des fluorocarbones, des hydrofluorocarbones, des éthers fluorés et des gaz atmosphériques.

6. Procédé suivant la revendication 1, dans lequel le point d'ébullition normal du constituant à point d'ébullition le plus élevé des fluides réfrigérants multiconstituants (105, 110) est supérieur d'au moins 50 K au point d'ébullition normal du constituant à point d'ébullition le plus bas du fluide réfrigérant multiconstituant.

7. Procédé suivant la revendication 1, dans lequel les fluides réfrigérants multiconstituants (105, 110) comprennent au moins deux constituants choisis dans le groupe consistant en C_5F_{12}, CHF_2-O-C_2HF_4, C_4HF_9, $C_3H_3F_5$, C_2F_5-O-CH_2F, $C_3H_2F_6$, CHF_2-O-CHF_2, C_4F_{10}, CF_3-O-$C_2H_2F_3$, C_3HF_7, CH_2F-O-CF_3, $C_2H_2F_4$, CHF_2-O-CF_3, C_3F_8, C_2HF_5, CF_3-O-CF_3, C_2F_6, CHF_3, CF_4, O_2, Ar, N_2, Ne et He.

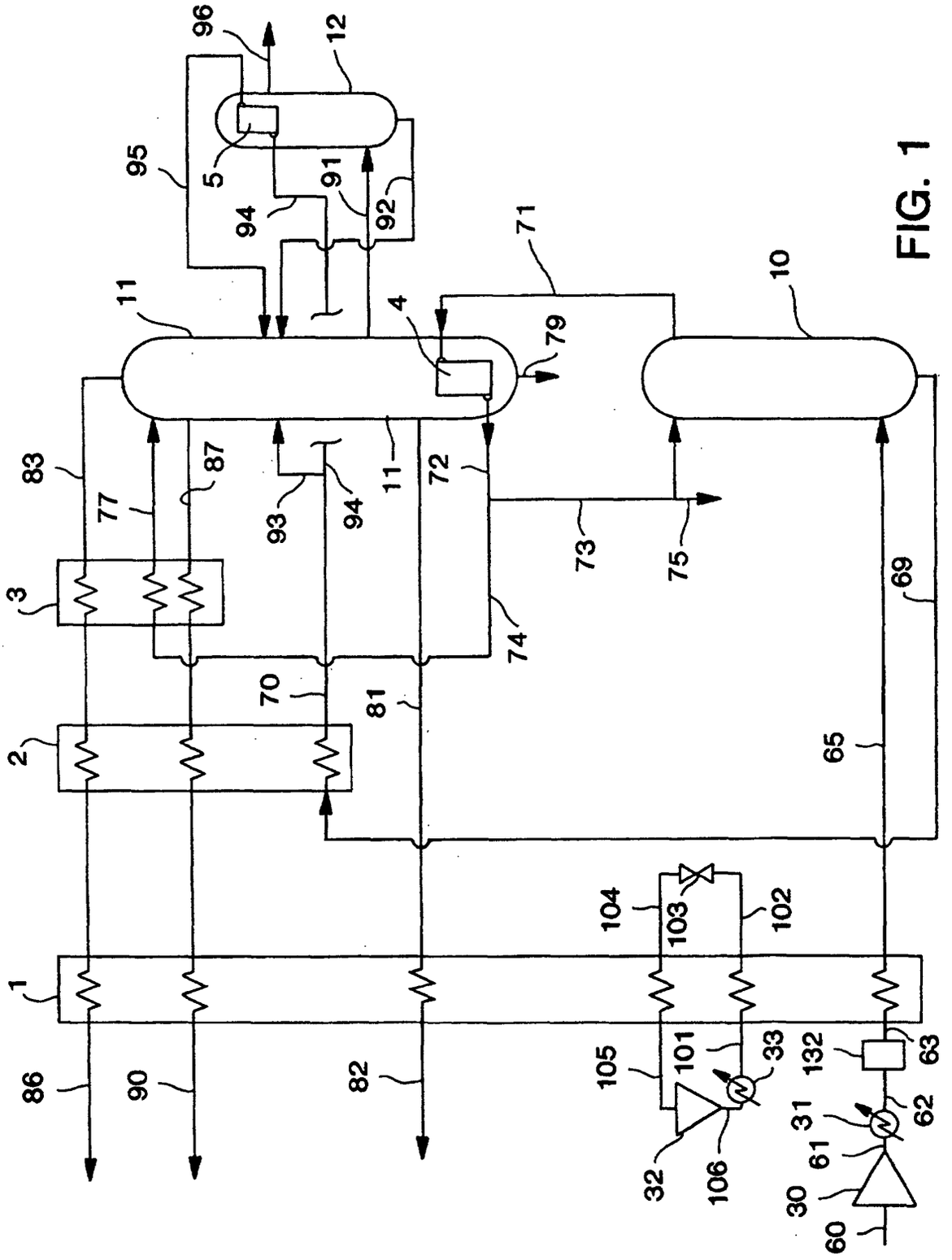
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FIG. 1

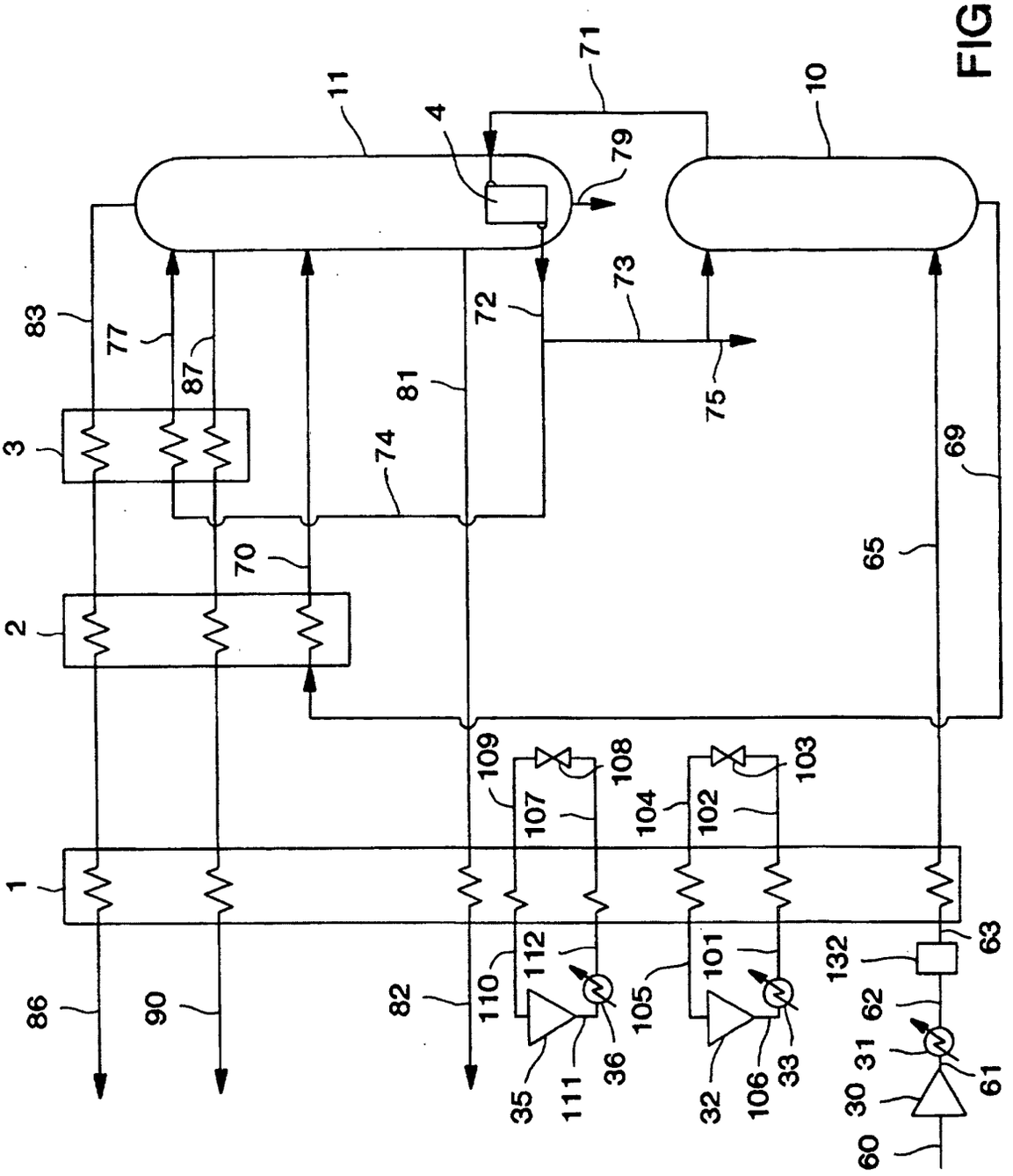
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FIG. 2